

# The Influence of the Phase Equilibria on the Critical Temperatures $T_c$ of the High- $T_c$ Bi-Sr-Ca-Cu-O and Y-Ba-Cu-O Compounds

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The phase equilibria of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$  (123 phase) strongly influence its oxygen content and consequently its critical temperature  $T_c$ . With increasing content of  $\text{BaCuO}_2$  or  $\text{CuO}$ ,  $T_c$  decreases. Whereas, if  $\text{Y}_2\text{BaCuO}_5$  (211 phase) is in equilibrium with the 123 phase, the oxygen content and  $T_c$  of which is high.  $\text{Bi}_{2+x}(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+d}$  exhibits an extended single phase region and its  $T_c$  is strongly affected by its chemical composition. In addition, the oxygen content of the phase is a function of the temperature and influences the  $T_c$  of the phase.

**Key words:** BSCCO, critical temperature, crystal chemistry, phase equilibria, YBCO

## INTRODUCTION

Due to the present phase equilibria at a given temperature, the chemical composition of any phase of a system may vary depending on the extension of its single phase region. In addition, its physical properties may vary, if they depend on the chemical composition of the compound. Considering this fact, it is important to determine to what extent the chemical compositions of the high-temperature superconducting solid solutions of the systems Bi-Sr-Ca-Cu-O ( $\text{Bi}_{2+x}(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+d}$ , 2212 phase,  $T_c \leq 94\text{K}$ ;  $\text{Bi}_{2+x}(\text{Sr,Ca})_4\text{Cu}_3\text{O}_{10-d}$ , 2223 phase,  $T_c = 110\text{K}$ ),<sup>1</sup> and Y-Ba-Cu-O ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ , 123 phase,  $T_c \leq 93\text{K}$ )<sup>2</sup> influence their critical temperatures  $T_c$ .

As the high- $T_c$  phases are oxides, it is necessary and important to point out, that besides a component, oxide is an equilibrium phase of the systems taking part in the phase equilibria of the high- $T_c$  superconducting phases. Reflecting this fact, it has to be considered that the oxygen contents of the high- $T_c$  phases and their critical temperatures may depend on the present phase relations of the prepared sample.

Contributing these considerations, it has to be determined to what extent the phase equilibria of the high- $T_c$  phases affect the cation concentrations and the oxygen contents of the high- $T_c$  phases, which may influence their critical temperatures. On the other hand, the question arises whether it is possible to fix the highest  $T_c$  by fixing the optimum chemical composition of the high- $T_c$  phases.

## EXPERIMENTAL

The samples of the Y-Ba-Cu-O system were calcined at 880 and 950°C for 24 h and sintered at 950°C for 24 h in flowing, high purity oxygen. After sintering, the samples were cooled down to 400°C and subsequently annealed at 400°C for 10 h in flowing high purity oxygen and air quenched. The samples of the Bi-Sr-Ca-Cu-O system were calcined at 750, 800, and 820°C and sintered at various temperatures between 780 and 900°C in air. The samples were air quenched, as well as furnace cooled after sintering. The critical temperatures ( $T_c$  onset) of the samples were determined by AC-susceptibility measurements. Due to the two-phase and three-phase character of the prepared samples, it is not possible to determine the oxygen content of the 123 phase directly. How-

**Table I.  $T_c$  and Volume Content of the Secondary Phase of the Prepared Samples**

Sample	$T_{c, \text{onset}}$ (K)
Single phase 123 sample	93
5 vol.-%CuO	91
10 vol.-%CuO	89
20 vol.-%CuO	87
5 vol.-%BaCuO <sub>2</sub>	88
10 vol.-%BaCuO <sub>2</sub>	85
20 vol.-%BaCuO <sub>2</sub>	69
25 vol.-%211	92
50 vol.-%211	93
30 vol.-%BaCuO <sub>2</sub> ,	
30 vol.-%211, 40 vol.-%123	93

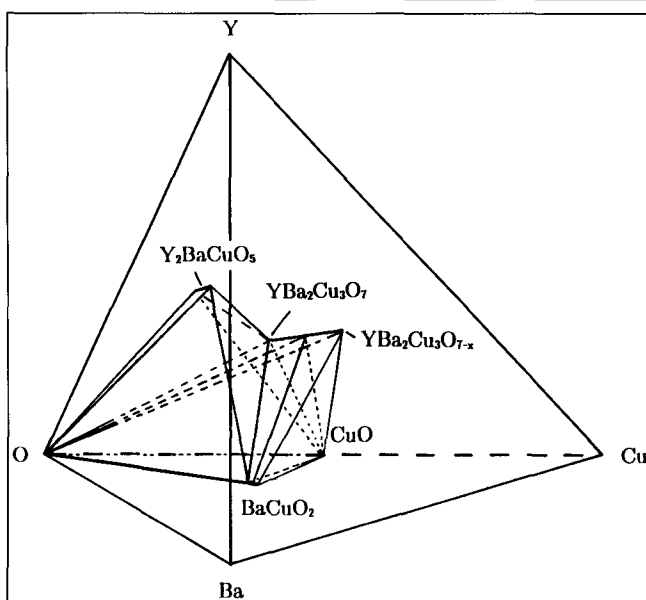


Fig. 1. Phase relations between oxygen, 123 phase, 211 phase, BaCuO<sub>2</sub>, and CuO (schematically).

ever, as  $T_c$  is a function of the oxygen content of the 123 phase,<sup>3</sup> it is concluded that a low  $T_c$  indicates a decreased oxygen content of the phase.

## RESULTS AND DISCUSSIONS

### The Y-Ba-Cu-O System

As it is indicated in Table I, the  $T_c$  of the CuO and BaCuO<sub>2</sub> containing samples is lower than the  $T_c$  of the single phase 123 sample. In addition, the  $T_c$ , as well as the oxygen content of the 123 phase, is a function of the volume content of CuO or BaCuO<sub>2</sub> of the prepared sample. With increasing volume content of CuO or BaCuO<sub>2</sub>, the  $T_c$  of the 123 phase decreases. Whereas, the  $T_c$  and the oxygen content of the 123 phase appears to be not affected by the 211 phase and is as high as the  $T_c$  of the single phase sample even at very high volume content of the 211 phase. In addition, the  $T_c$  of the 123 phase remains high even if BaCuO<sub>2</sub> or CuO is present as a fourth phase besides the 211 phase and oxygen. Therefore, highest  $T_c$  of the 123

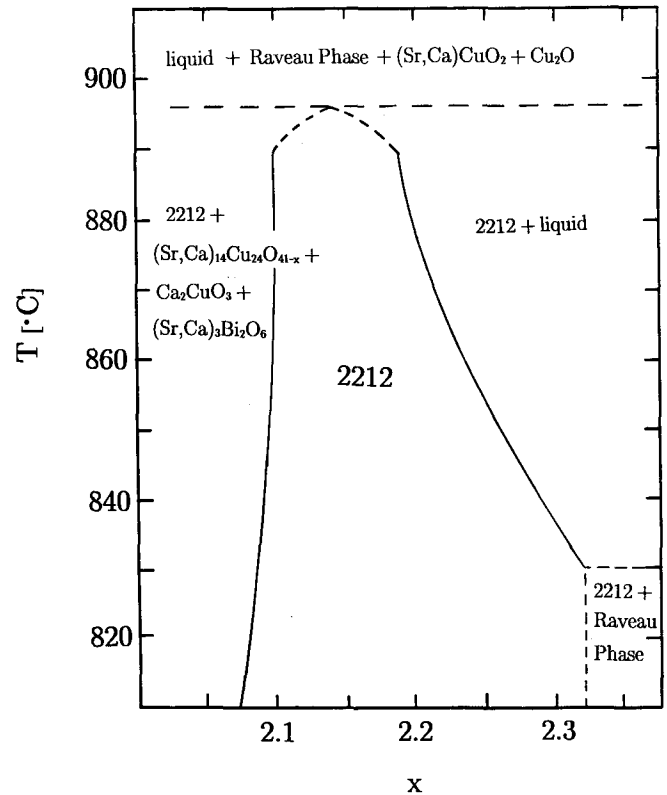


Fig. 2. The single phase region of the 2212 phase in a temperature vs concentration plot considering varying Bi-contents of the 2212 phase.

phase is fixed by preparing 211 phase containing samples, as it is generally done for the preparation of melt texture growth (MTG) Y-Ba-Cu-O ceramics.<sup>3</sup> These observations are compiled in form of a phase diagram in Fig. 1.

### The Bi-Sr-Ca-Cu-O System

In contrast to the 2223 phase, the 2212 phase of the system Bi-Sr-Ca-Cu-O exhibits an extended single phase region.<sup>4-6</sup> Therefore, the second part of this article is focused on the 2212 phase.

The 2212 phase exhibits varying contents of Bi, Sr, and Ca as it is shown in Figs. 2 and 3. The Bi content varies between 2.1 and 2.3 at low temperatures (Fig. 2). With increasing temperatures, the Bi variation decreases. At 895°C in air, the critical formal unit of Bi is about 2.18. In addition, the variation of the Sr/Ca ratio of the 2212 phase decreases with increasing temperatures (Fig. 3); and at 895°C, the critical Sr/Ca ratio of the 2212 phase is about 2/1. Therefore, at 895°C the critical composition of the 2212 phase is very close to the composition Bi<sub>2.18</sub>Sr<sub>2</sub>Ca<sub>1</sub>Cu<sub>2</sub>O<sub>8+d</sub>. Within this extended single phase region, the  $T_c$  of the phase varies significantly as it is shown in Figs. 4 and 5. With increasing Bi (Fig. 4) and Ca content (Fig. 5) of the 2212 phase its  $T_c$  decreases even at different sintering temperatures.

The oxygen content of the 2212 phase is also a function of the temperature as it is indicated in Fig. 6.

Between 780 and 890°C with increasing temperatures, its oxygen content decreases. This has been determined by thermogravimetric measurements. The

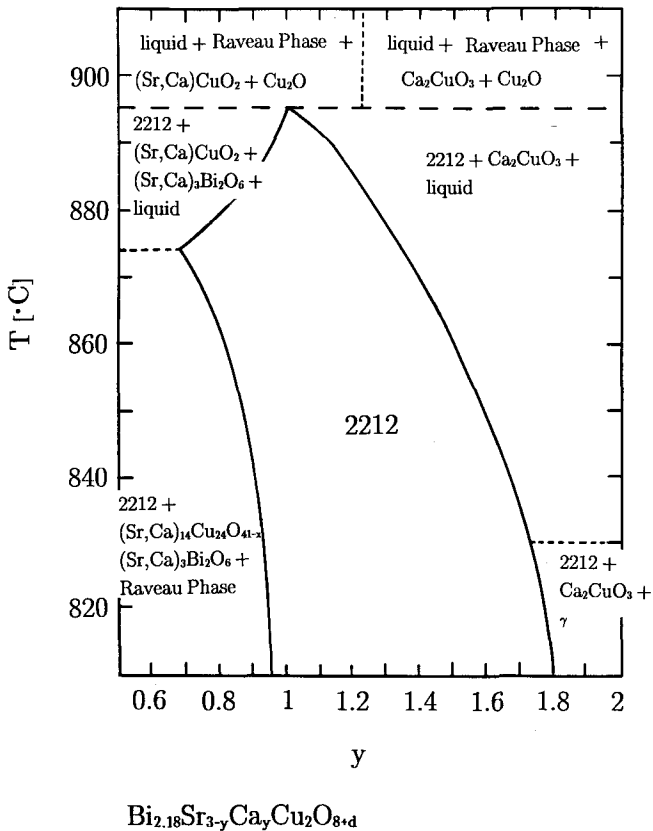


Fig. 3. The single phase region of the 2212 phase in a temperature vs concentration plot considering varying Ca-contents of the 2212 phase.

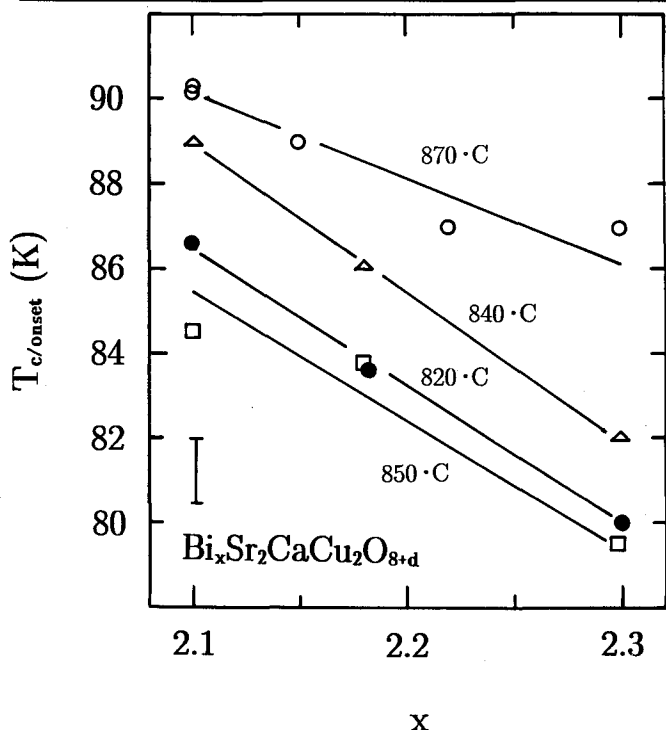


Fig. 4.  $T_{c\text{-onset}}$  vs Bi-content of the 2212 phase.  $T_c$  decreases with increasing Bi-content.

$T_c$  of the 2212 phase increases with increasing temperatures or decreasing oxygen content up to 870°C and then decreases again. Contributing these results, it is concluded that highest  $T_c$  of the 2212 phase is reached at 870°C in air, corresponding to a certain oxygen content of about 8.2,<sup>7</sup> and Sr-rich composition.

In samples containing  $\text{Ca}_2\text{CuO}_3$ ,  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41-x}$ ,  $\text{CuO}$ ,  $(\text{Sr,Ca})_3\text{Bi}_2\text{O}_6$ ,  $(\text{Sr-Bi}) \gamma$ , or the Raveau phase ["2201" phase] as secondary phases beside the 2212 phase, no influence of the phases on the  $T_c$  has been observed, even for high volume contents up to 50% of the secondary phases.

### CONCLUSION

Our conclusions are as follows:

- $T_c$  is a function of the chemical composition of the HT $_c$  phases  $\text{Bi}_{2+x}(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+d}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .
- It is possible to fix the highest  $T_c$  of the phases by considering today's knowledge of the phase equilibria of the systems Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O.
- Within the 2212 single phase region, the oxygen content, as well as those of the cations Bi, Ca, and Sr, can be changed substantially.

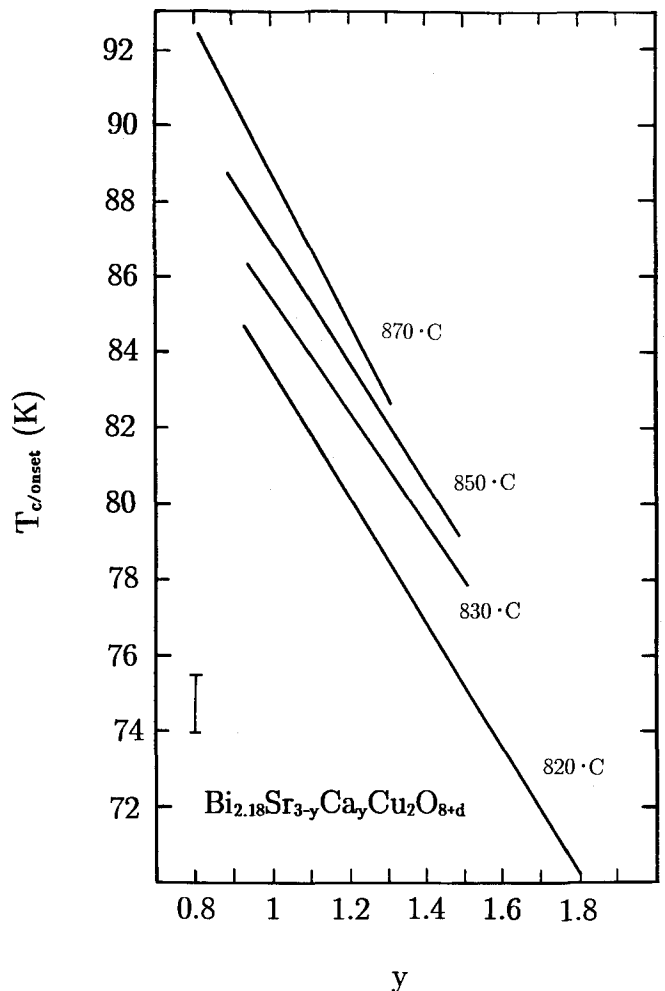


Fig. 5.  $T_{c\text{-onset}}$  vs Ca-content of the 2212 phase.  $T_c$  decreases with increasing Ca-content.

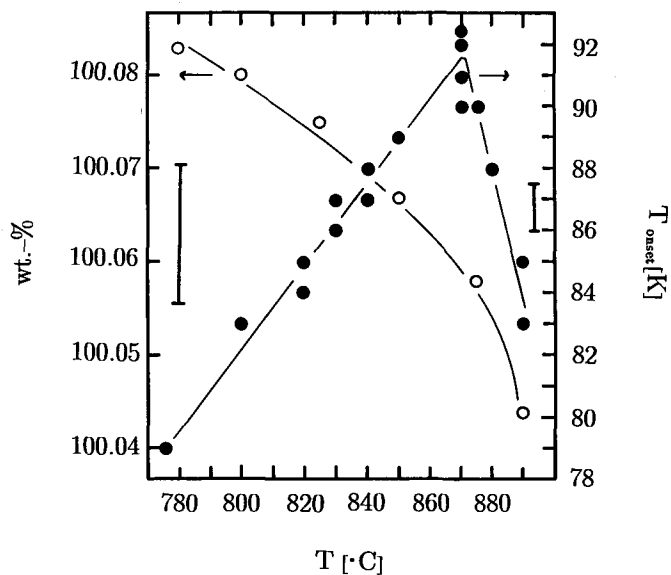


Fig. 6. Oxygen content of the 2212 phase vs temperature determined by thermogravimetric measurements (circles) and  $T_c$  vs temperature (dots). Highest  $T_c$ , reached at 870°C in air, corresponds with a certain oxygen content of the phase.

- Within the 123 single phase region, the oxygen content can be changed even at constant oxygen partial pressure.

Considering these conclusions, it has to be pointed out that besides the synthesis of new layered cuprates, the determination of their single phase regions and the single phase regions of already known layered cuprates is also necessary in order to optimize high temperature superconductors.

#### REFERENCES

1. H. Maeda, Y. Tanaka, M. Fukotomi, T. Asano, K. Togano, H. Kumakura, M. Uehara, S. Ikeda, K. Ogawa, S. Horiuchi and Y. Matsui, *Physica C* 153–155, 602 (1988).
2. M.K. Wu, J.A. Ashburn, C.J. Torng, P.-H. Hor, R.L. Mong, L. Gao, Z.J. Huang, Q. Wang and C.W. Chu, *Phys. Rev. Lett.* 58, 908 (1987).
3. M. Murakami, H. Fujimoto, S. Gotho, K. Yamaguchi, N. Koshizuka and S. Tanaka, *Physica C* 185–189, 321 (1991).
4. B. Hong and T.O. Mason, *J. Am. Ceram. Soc.* 74, 1045 (1991).
5. P. Majewski and B. Hettich, *MRS* 275, 627 (1992).
6. T.G. Holesinger, D.J. Miller, L.S. Chumbley, M.J. Kramer, K.W. Dennis, *Physica C* 202, 109 (1992).
7. J. Bock and E. Preisler, *Proc. of the Int. Cryogenic Materials Conference on High-Temperature Superconductors—Materials Aspects* (8–11 May 1990, Garmisch-Partenkirchen, F.R.G., DGM, Oberursel, 1991), p. 215.